New Layered Nanolaminates for Use in Lithium Battery Anodes

Prof. Yury Gogotsi (PI)
Prof. Michel Barsoum (Co-PI and Presenter)

Drexel University,
Philadelphia, PA, USA.

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Project ID # ES146

Overview

Timeline

- Project start date: Jan. 2011
- Project end date: Dec. 2014
- Percent complete: 50%

Budget

- Total project funding
  – $1M
- Funding received in FY12: $245K
- Funding for FY13: $399K
- Total funding received: $773K

Barriers

- Barriers addressed
  A. Short life-span of modern batteries
  B. Low charge density
  C. Compromised safety

Partners

Externally supported collaborations

- Oak Ridge National Laboratory, Dr. Ed Hagaman and Dr. Sheng Dai
- University of Pennsylvania, Prof. Vivek Shenoy
- Paul Sabatier University, Toulouse, France, Prof. Patrice Simon
- Linkoping University, Sweden Dr. Lars Hultman

Technical Objectives and Technical Approach

- **Objectives of this Study:**

  Replace graphite with a new material. Layered binary carbides and nitrides known as MXenes, where the A-group element is selectively etched from the MAX phases – the latter ternary layered carbides and nitrides - may offer combined advantages of graphite and Si anodes with a higher capacity than graphite, less expansion, longer cycle life and a lower cost than Si nanoparticles.

Milestones for FY12

Month/Year	Milestone
March 2012	Reduce the particle size of MAX phase to submicrometer level and demonstrate a correlation between the particle size and the Li uptake capacity. (Mar. 12) **Canceled -** due to change in research direction to concentrate on MXenes (exfoliated MAX phases) instead of pristine MAX phases.
September 2012	Fully remove the A-group layers from the MAX phases to produce graphene-like 2-D structure which we labeled "MXene" and study its effect on electrochemical behavior as anodes Li-ion batteries. **Completed**
September 2012	Produce MXene anodes with the capacity of about 80 % of commercial graphite anodes. **Completed**
September 2012	Investigate the effect of different carbon additives on the performance of MXene anodes and define the best additives. **Completed**

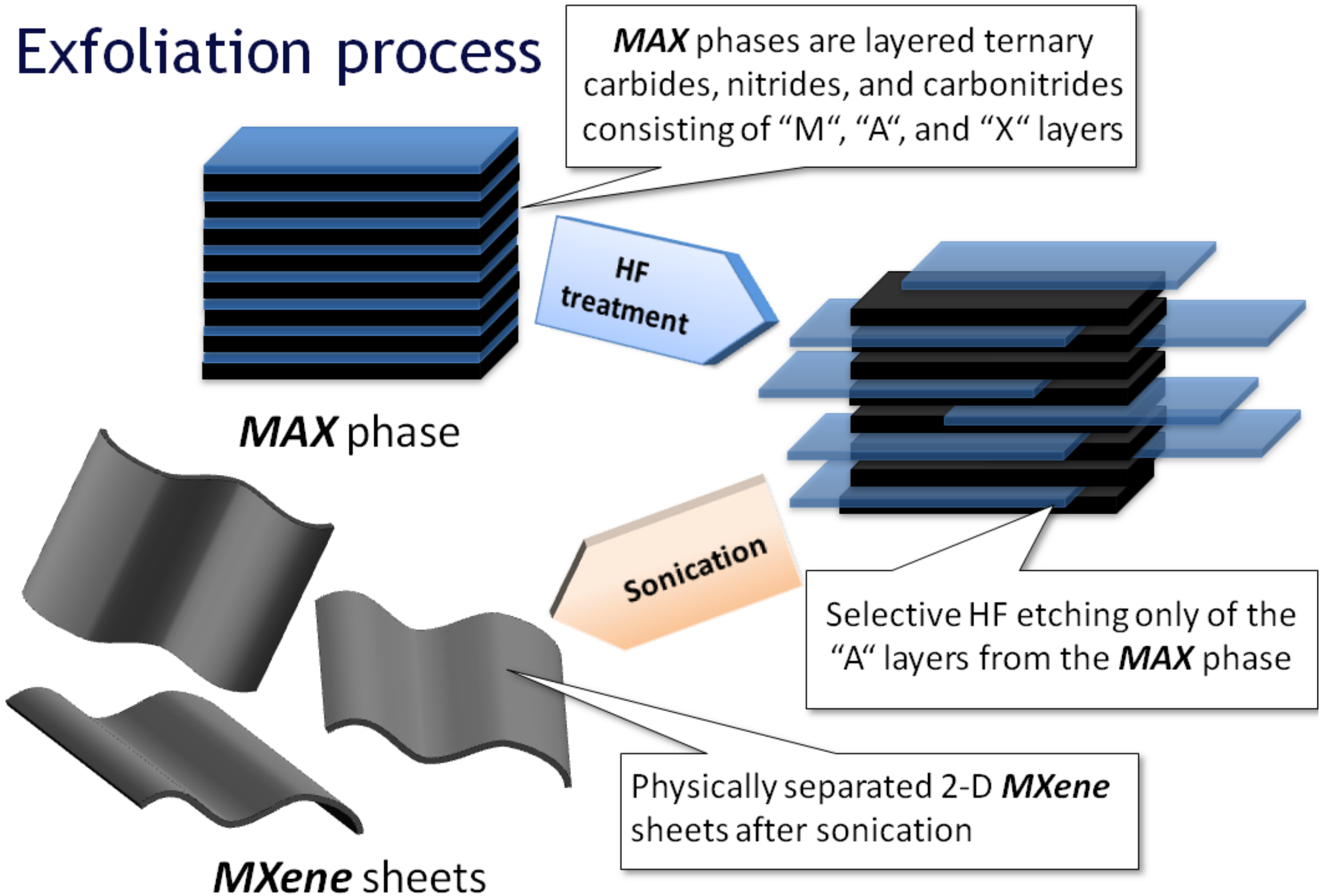
Milestones for FY13

Month/Year	Milestone
December 2012	Select the best carbon additive and binder that results in the highest Li uptake for selected MXenes. **Completed**
June 2013	Develop higher volumetric capacity anodes for LIBs than the commercial anodes. **Ongoing**
September 2013	Produce MXenes of new chemistries (such as Nb_2C, V_2C) that can achieve anode capacities of 400 $mAhg^{-1}$ at cycling rates of 1C or faster. **Ongoing**
December 2013	Produce MXene anodes with capability of delivering a stable performance at 10 C cycling rates. **Ongoing**

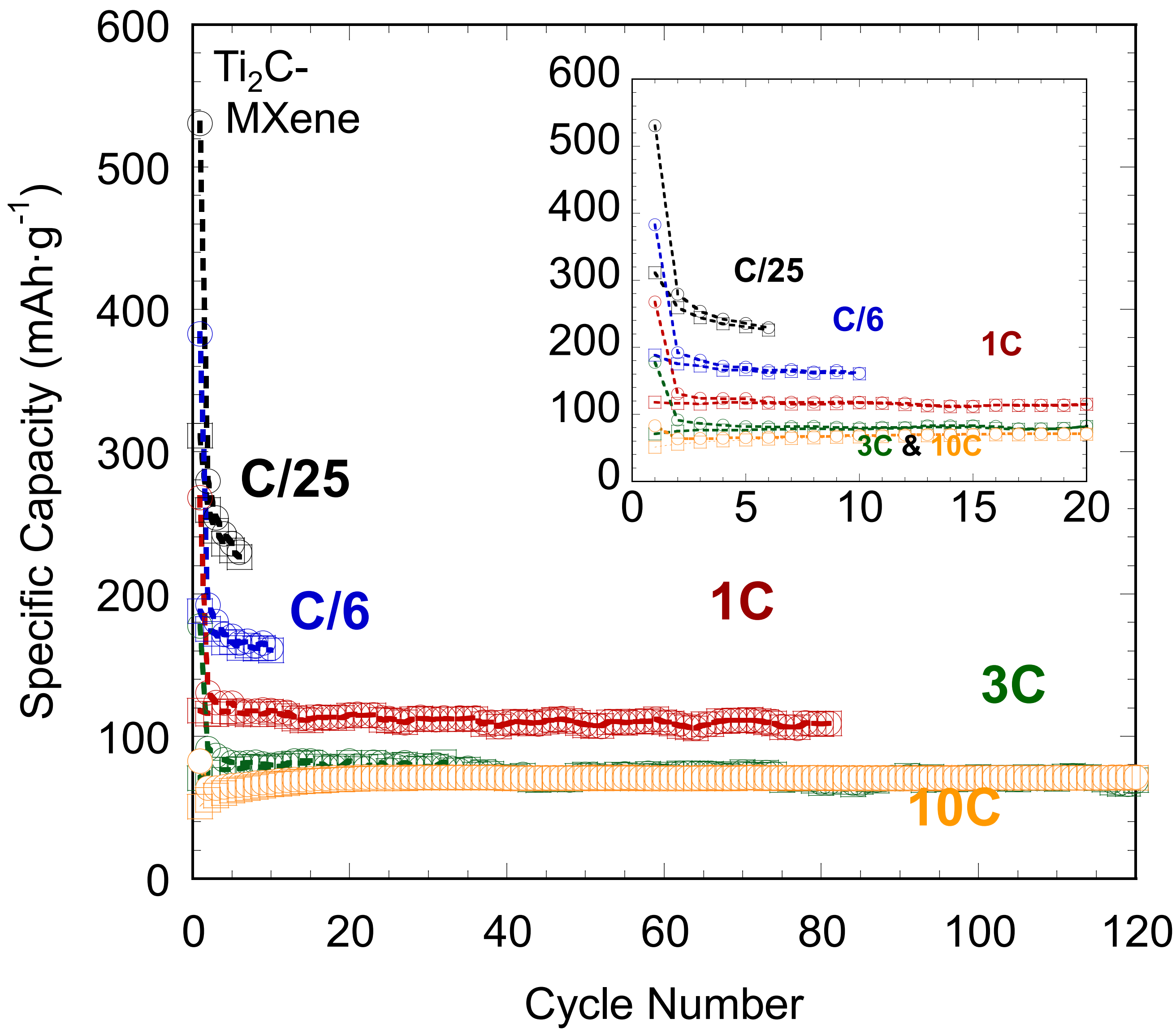
Approach/Strategy

- Rapid screening of as many MXenes as possible shall be carried out to identify the most promising chemistry, by testing their performance in LIBs.
- Study the effect of carbon and binder additives on the performance of MXene and attempt to produce binder-free electrodes.
- Study the lithiation and delithiation mechanisms and the solid-electrolyte interfaces (SEI) in order to enhance the performance of MXenes; e.g. minimize the first cycle irreversibility.

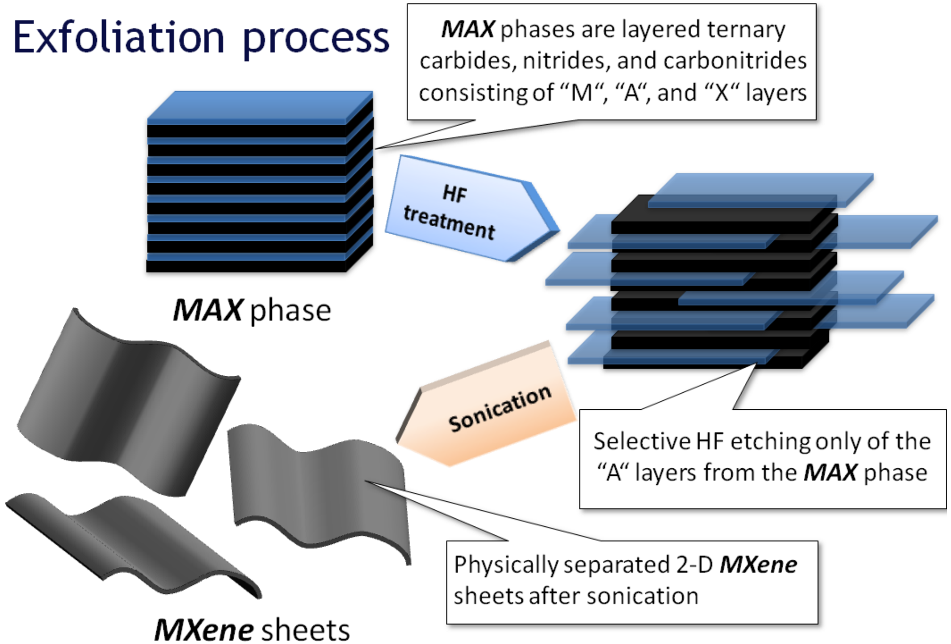
Technical Accomplishments (Previously Presented)

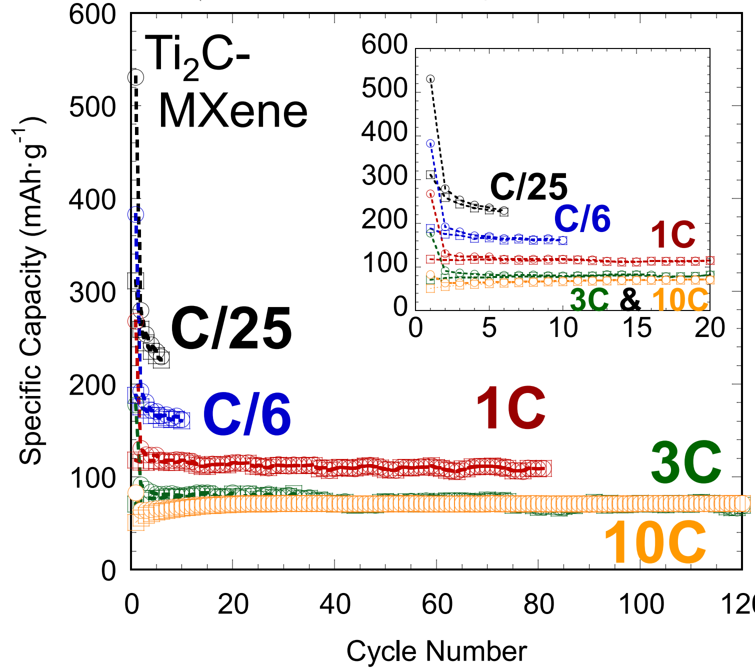


M. Naguib, *et al.* Advanced Materials 23 (2011) 4248-4253 | M. Naguib, *et al. ACS Nano* 6 (2012) 1322-1331
M. Naguib, *et al. Electrochemistry Communications* 16 (2012) 61-64


Ti2C-MXene
Specific Capacity (mAh·g-1)
Cycle Number
C/25
C/6
1C
3C
10C
3C & 10C
0
100
200
300
400
500
600
0
20
40
60
80
100
120
0
5
10
15
20

Technical Accomplishments (Previously Presented)





- Selective etching of A out from MAX phases results in exfoliation of MX layers forming a new family of 2-D transition metals carbides and carbonitrides that we call "MXenes"
- Different MXenes [Ti_3C_2, Ti_2C, TiNbC, Ti_3CN, Ta_4C_3, $(V_{0.5}Cr_{0.5})_3C_2$] have been synthesized.
- Testing Ti_2C and Ti_3C_2 as anodes in LIBs showed reversible Li insertion in those materials.
- High cycling rates are possible, e.g. 120 mAh.g-at 1C in case of Ti_2C, and 80 mAh.g^{-1} at 10C.
- Preliminary results showed promising performance of Ti_2C, however first cycle irreversibility needs to be minimized and other MXenes should be explored.

M. Naguib, *et al.* Advanced Materials 23 (2011) 4248-4253 | M. Naguib, *et al. ACS Nano* 6 (2012) 1322-1331
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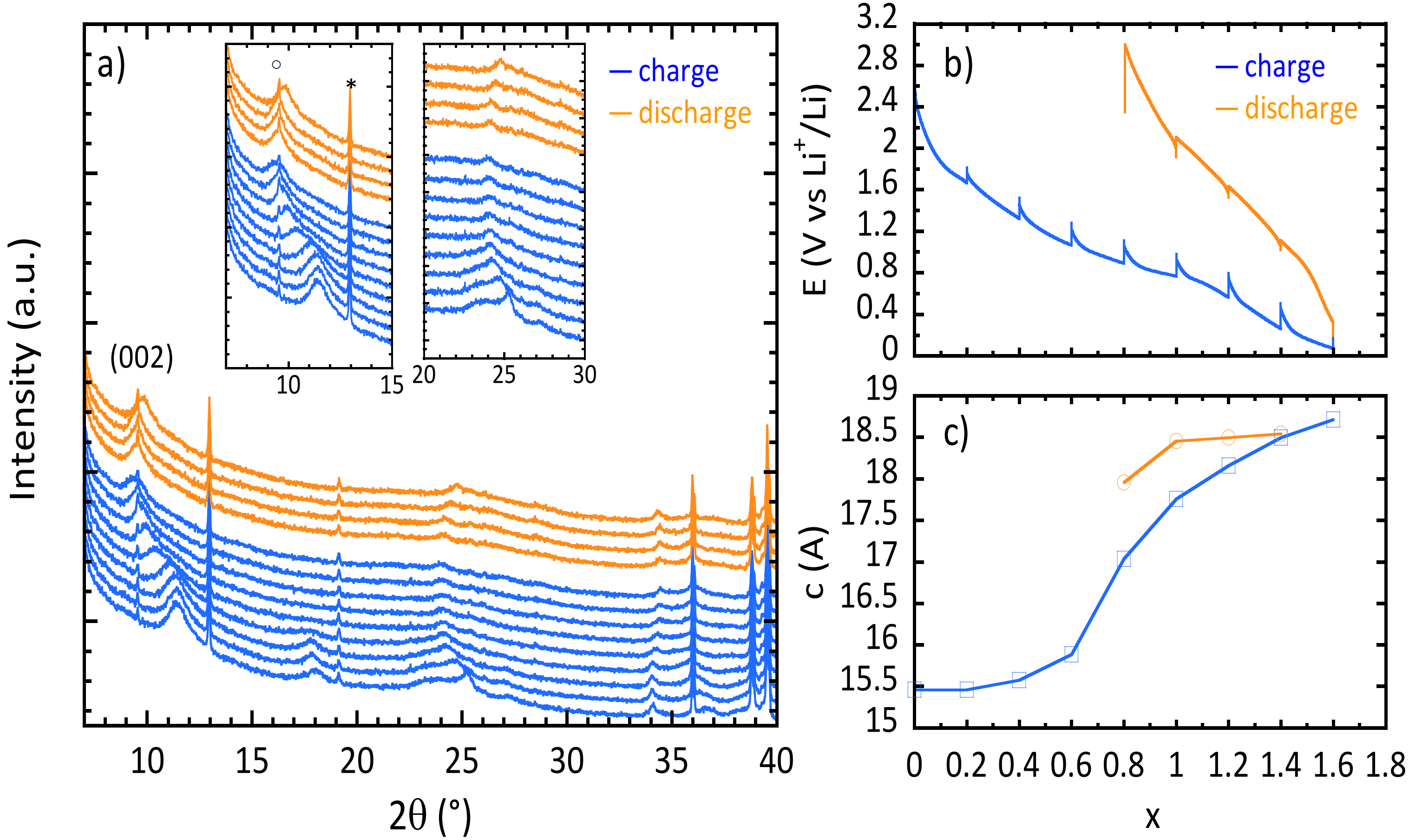
Technical Accomplishments

In-situ XRD for electrochemical lithiation and delithiation



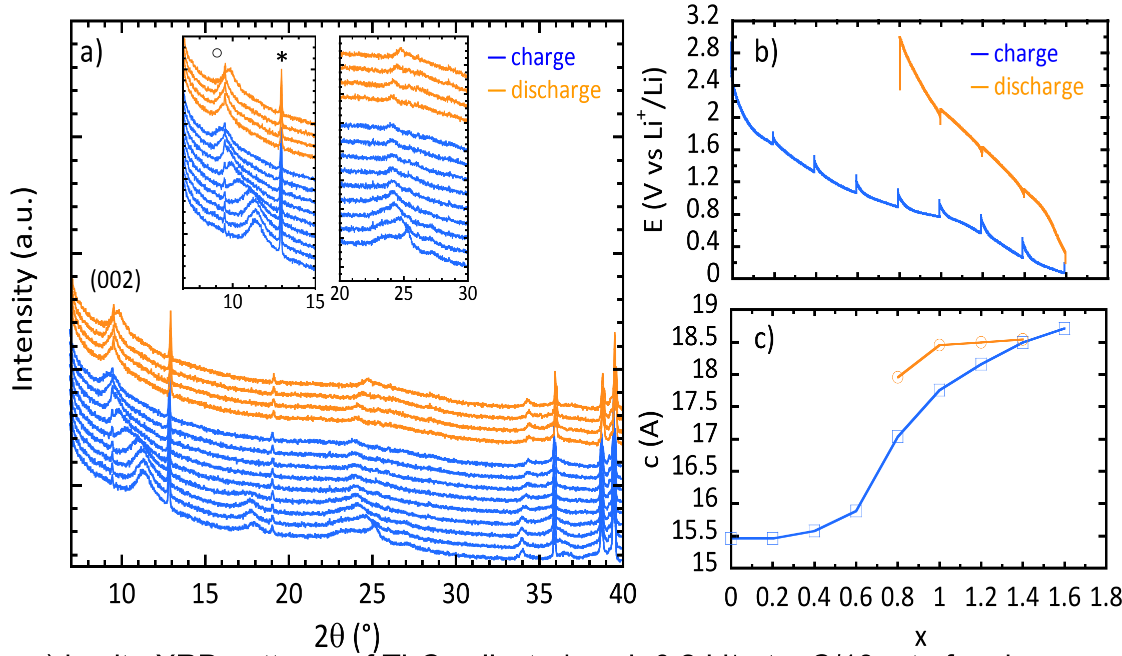
a) in-situ XRD patterns of Ti_2C collected each 0.2 Li^+ at a C/10 rate for charge and discharge, *: unreacted Ti_2AlC, ○: unreacted Ti_3AlC_2, b) corresponding constant current charge/discharge curve, and c) *c* parameter calculated from (002) peak shift during charge (black triangles) and discharge (open squares)

J. Come, *et al. Journal of The Electrochemical Society*, 159 (2012) 61-64

Technical Accomplishments

In-situ XRD for electrochemical lithiation and delithiation

- No new peaks appeared during lithiation, but a progressive downshift of the 002 peak was observed, corresponding to an increase of *c* lattice parameter.
- Based on XRD results, we conclude that the charge storage in Ti_2C – and by extension all other *MXenes* - is due to Li^+ intercalation between the Ti_2C layers and not due to a conversion reaction.



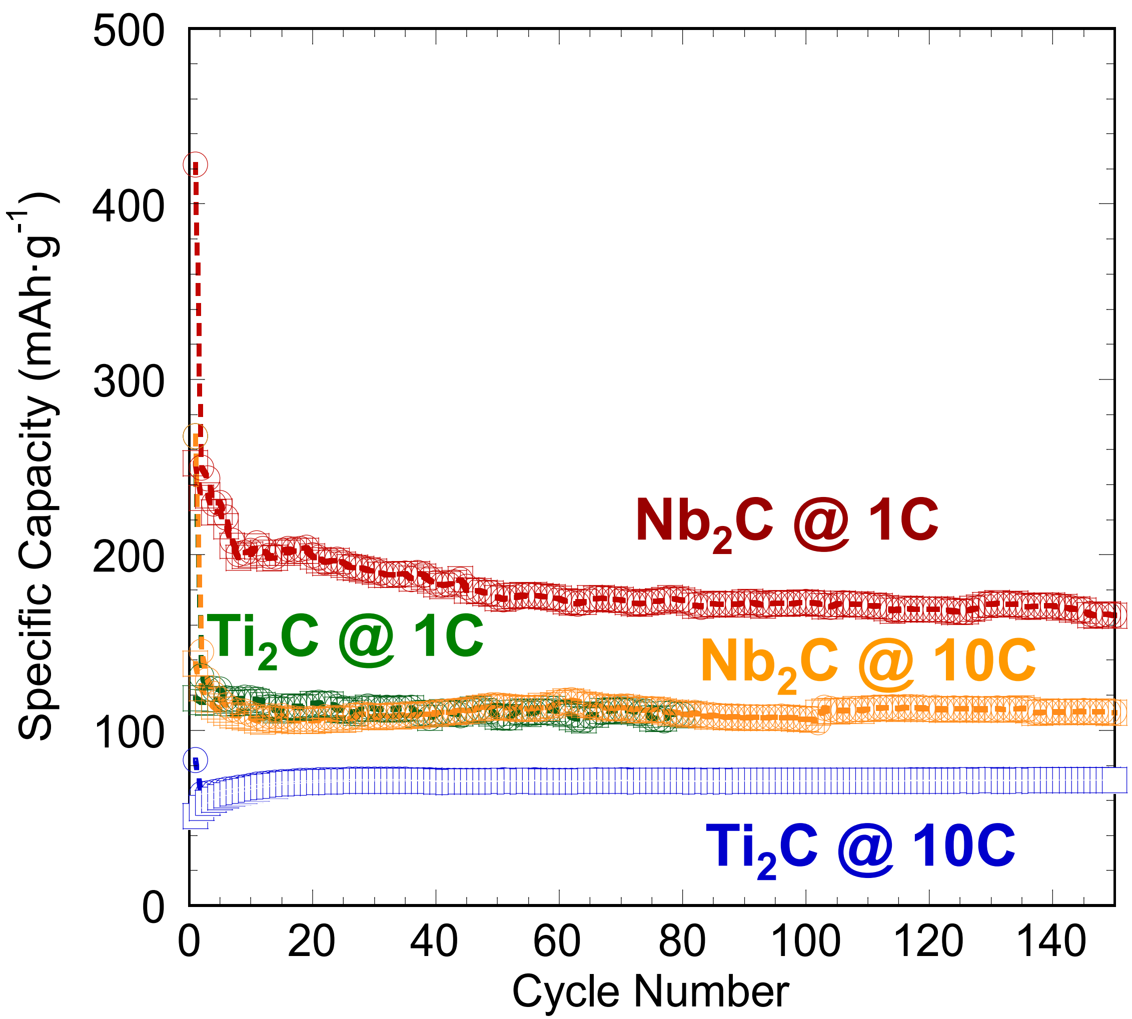
a) in-situ XRD patterns of Ti_2C collected each 0.2 Li^+ at a C/10 rate for charge and discharge, *: unreacted Ti_2AlC, ○: unreacted Ti_3AlC_2, b) corresponding constant current charge/discharge curve, and c) *c* parameter calculated from (002) peak shift during charge (black triangles) and discharge (open squares)

* An irreversibility in the *c* parameter can partially explain the 1st cycle irreversibility as the Li^+ ions get trapped between the *MXene* layers, in addition to SEI layer formation.

J. Come, *et al. Journal of The Electrochemical Society*, 159 (2012) 61-64

Technical Accomplishments

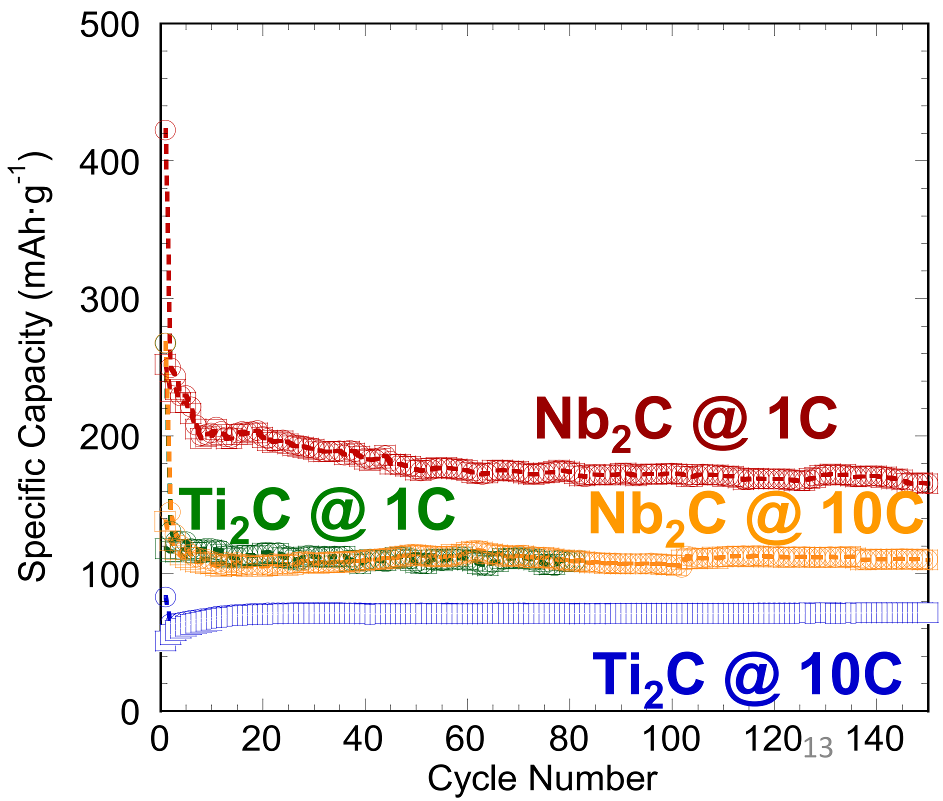
Other MXenes anodes



Technical Accomplishments

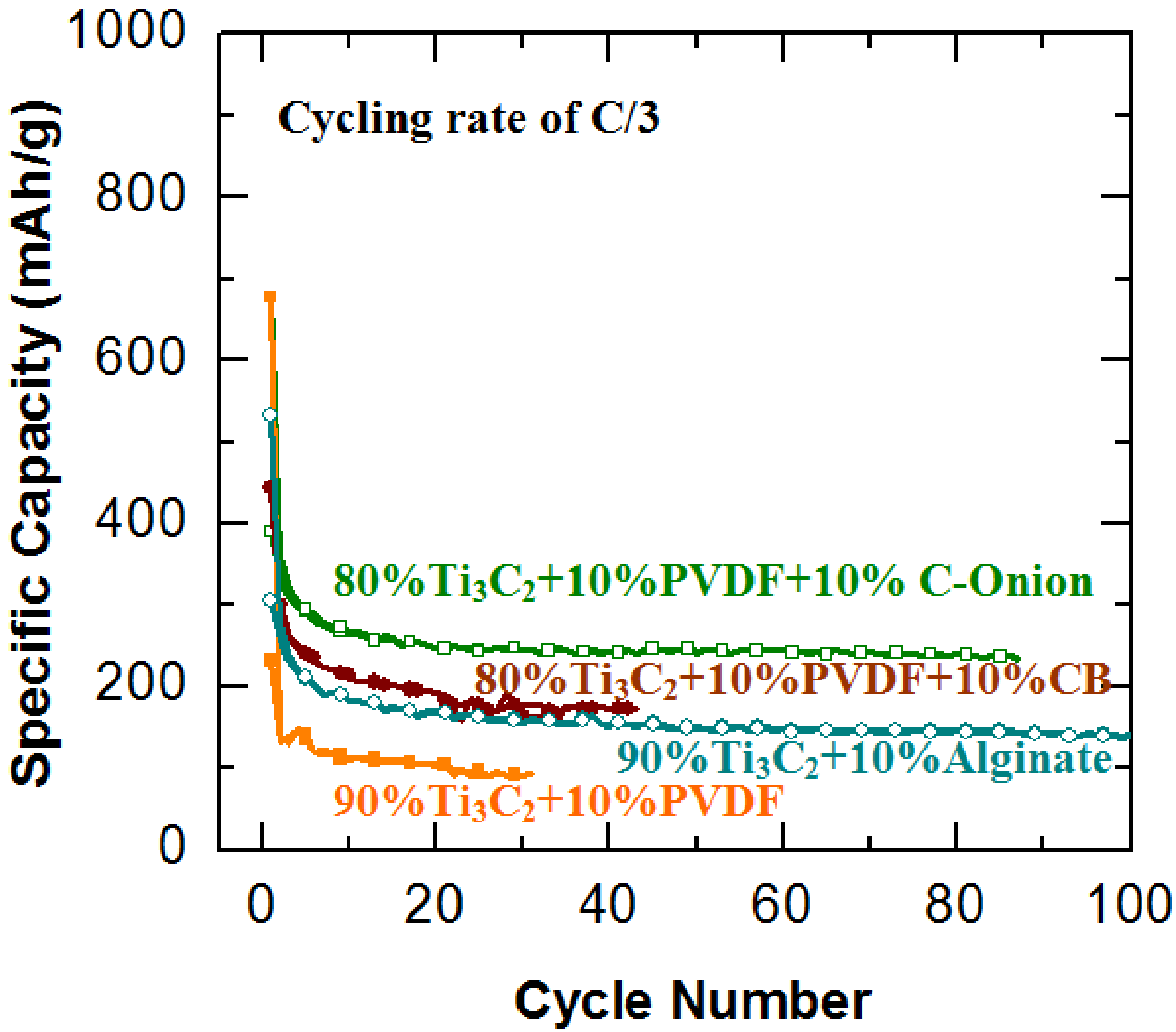
Other MXenes anodes

- In addition to Ti_2C and Ti_3C_2, other MXenes (i.e. Ta_4C_3 and Ti_3CN) were tested as anodes for LIBs.
- At a C/8 rate, stable capacity > 250 mAh/g was obtained for Ti_3CN; at 3C a stable capacity of 150 mAh/g was obtained after 150 cycles.
- Good volumetric capacity of 1400 mAh.cm^{-3} at C/3 was obtained for Ta_4C_3.
- Recently, we managed to synthesis Nb_2C by etching Al out of Nb_2AlC
- Nb_2C anodes performed better than Ti_2C. At a 1C rate, a stable capacity of 175 mAh/g was obtained. Even at 10 C, the reversible capacity was 110 mAh/g, which is close to that obtained for Ti_2C at 1C.
- Also, Nb_2C showed <u>*lower*</u> lithiation and delithiation voltages than Ti_2C.



Technical Accomplishments

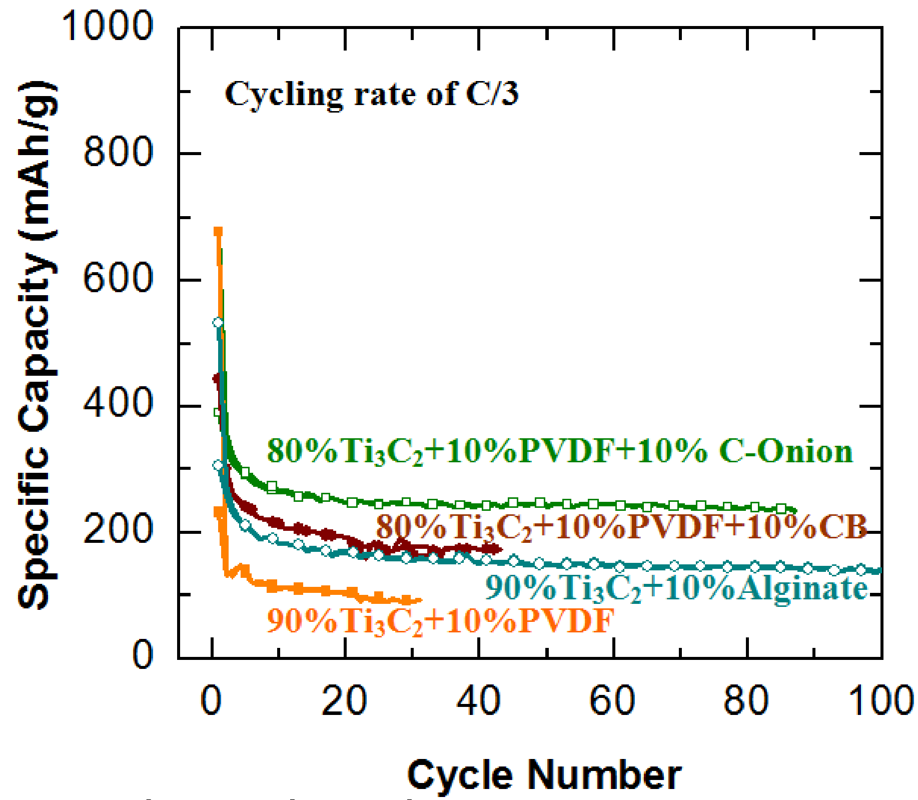
Effect of carbon and binder additives



Technical Accomplishments

Effect of carbon and binder additives

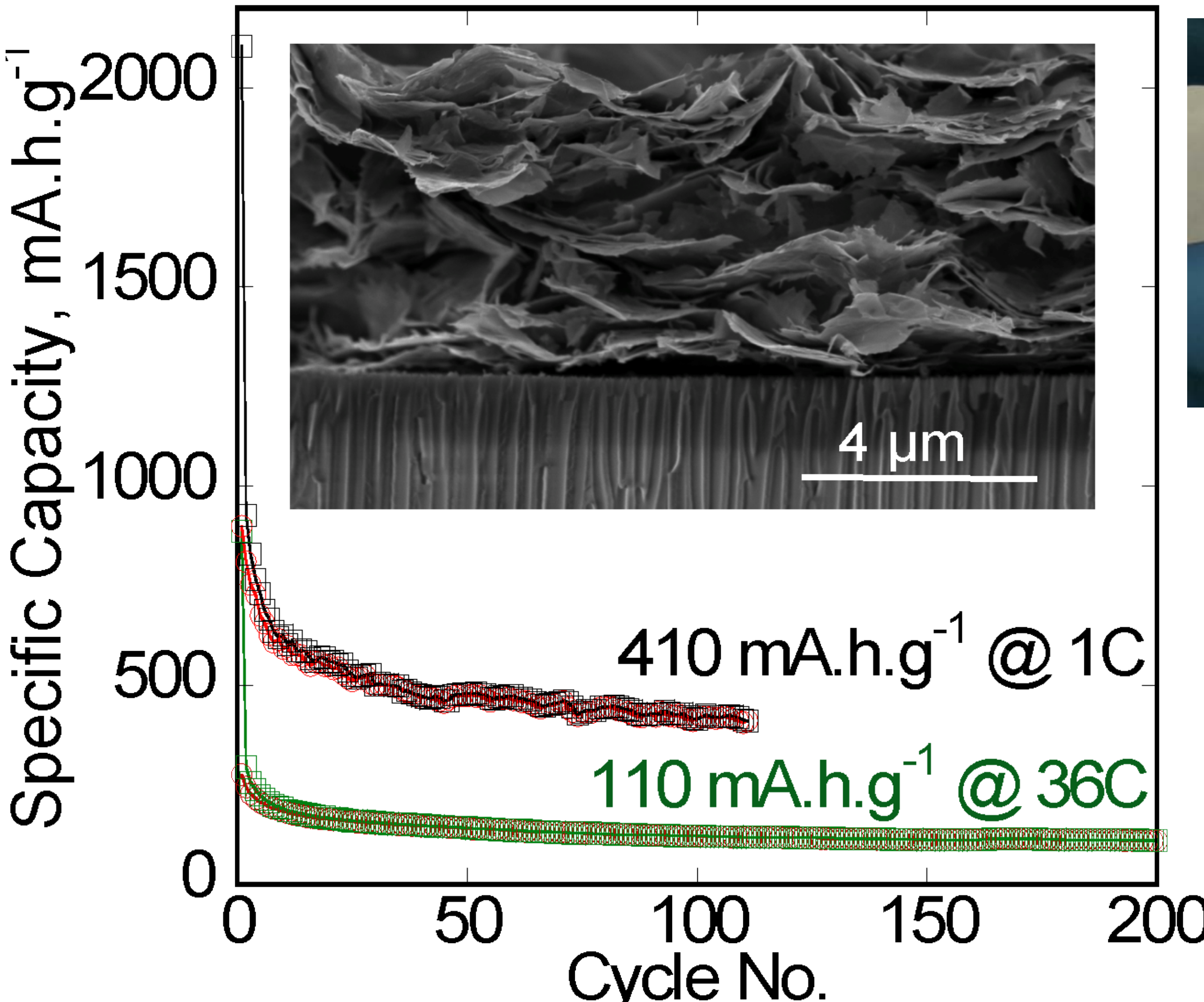
- The effect of various carbon additives in different forms (carbon black, carbon onions, nanotubes, and carbide derived carbon) on the performance of MXene anodes was studied. Different binders were also tested. Since Ti_3C_2 is the most studied MXene, it was used as the active material.
- Among the different binders, alginate (10 wt.%) yielded the best performance when no carbon additive was used. Adding 10 wt.% of carbon onions to PVDF resulted in a stable capacity of ≈ 240 mAh/g.

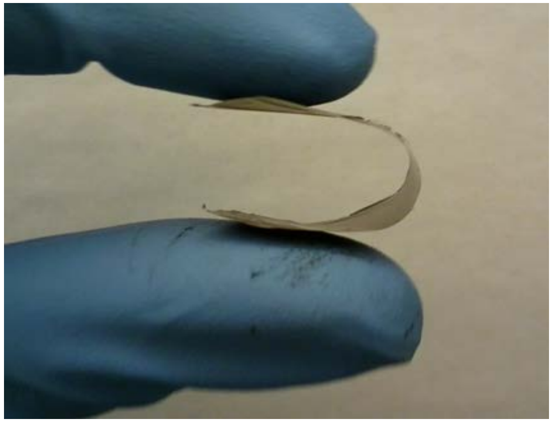


- The capacity increase can be explained by an enhanced conductivity.
- The highest capacity was obtained for a mixture of 80 wt.% Ti_3C_2, 10% PVDF & 10% C-onions.
- Since none of the binders performed better than additive-free anodes, this task was temporarily postponed.

Technical Accomplishments

Additive-free delaminated Ti_3C_2





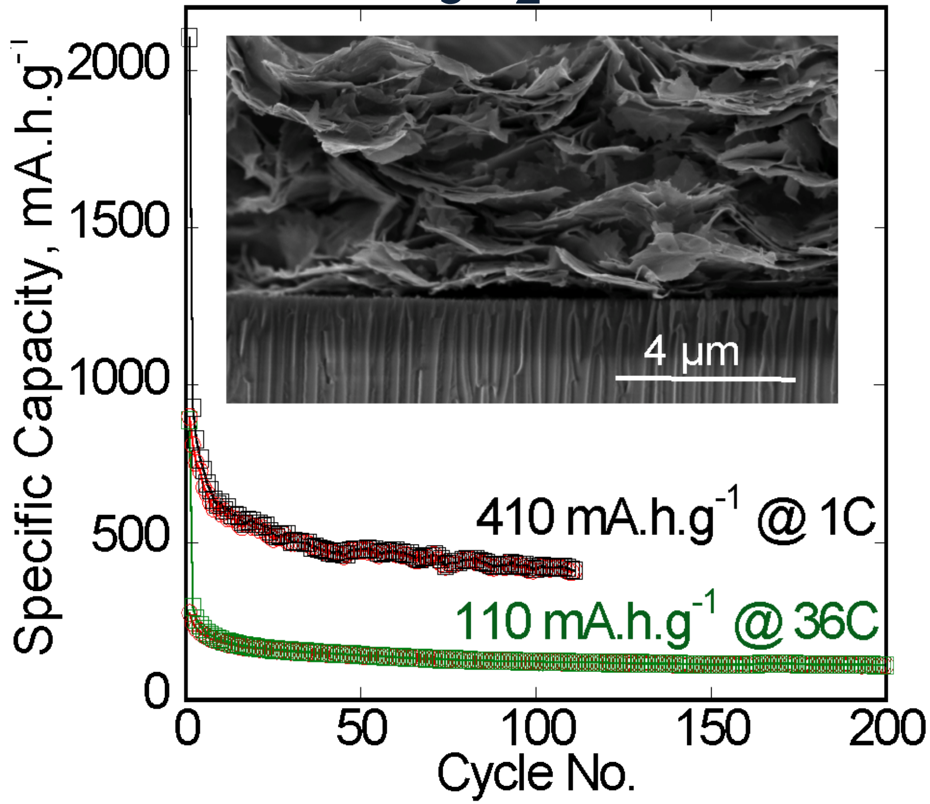
MXene Paper is *Flexible*

O. Mashtalir, *et al. Nature communications* (2013) DOI: 10.1038/ncomms2664

Technical Accomplishments

Additive-free delaminated Ti_3C_2

- Complete delamination of Ti_3C_2 has been successfully achieved. Additive-free Ti_3C_2 anodes (inset) were made by filtering a dispersion of delaminated flakes in water. They showed a capacity of 410 mAh/g at a 1C cycling rate after 100 cycles, and a capacity of 110 mAh/g at a cycling rate of 36 C for 200 cycles.
- Such rates are significantly faster than what graphite can handle.

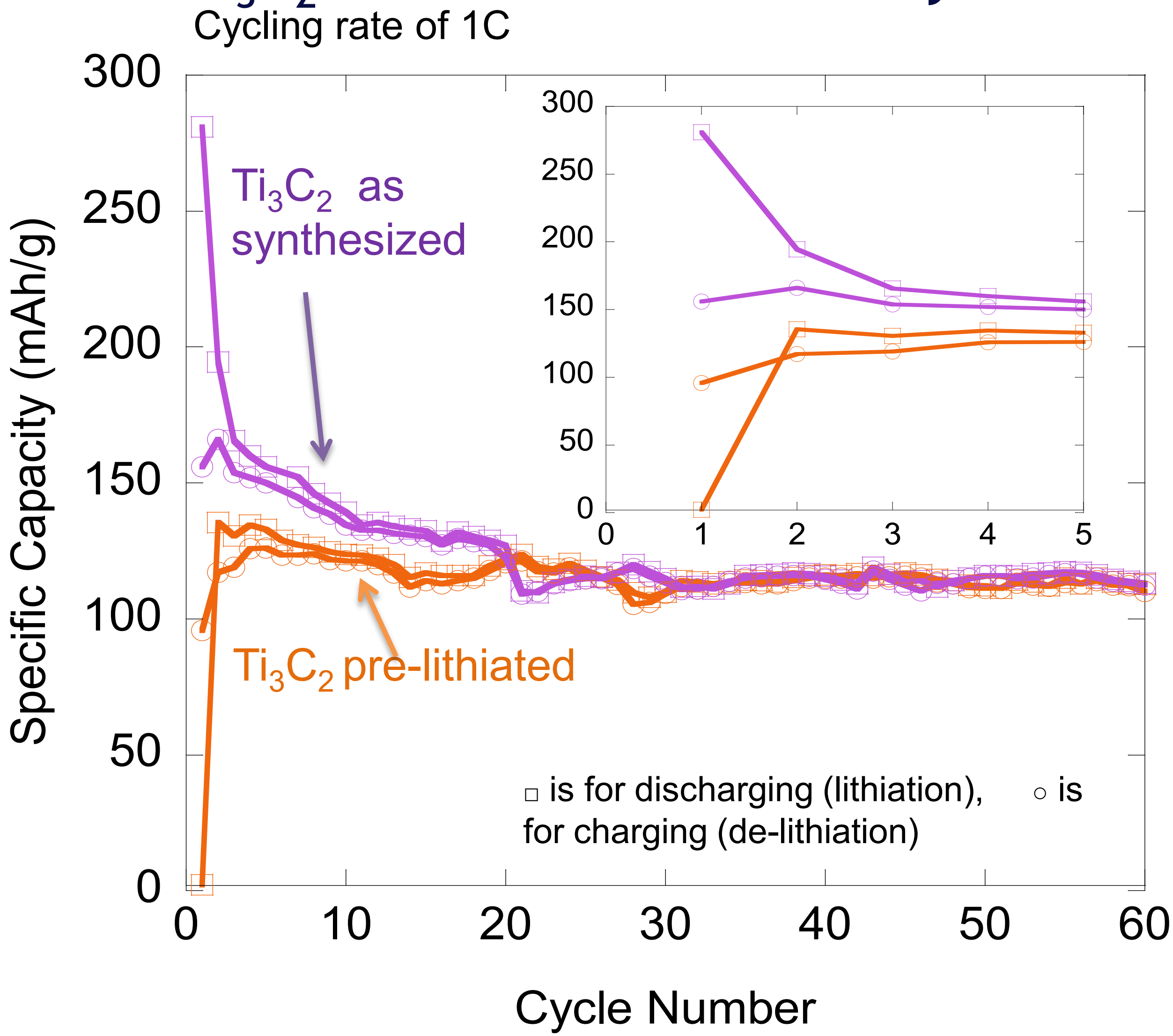


- Note that the results shown here were obtained on *additive free* – no binders or other additive – anodes. This feature should prove useful commercially in simplifying LIB design and containing costs.

O. Mashtalir, *et al. Nature communications* (2013) DOI: 10.1038/ncomms2664

Technical Accomplishments

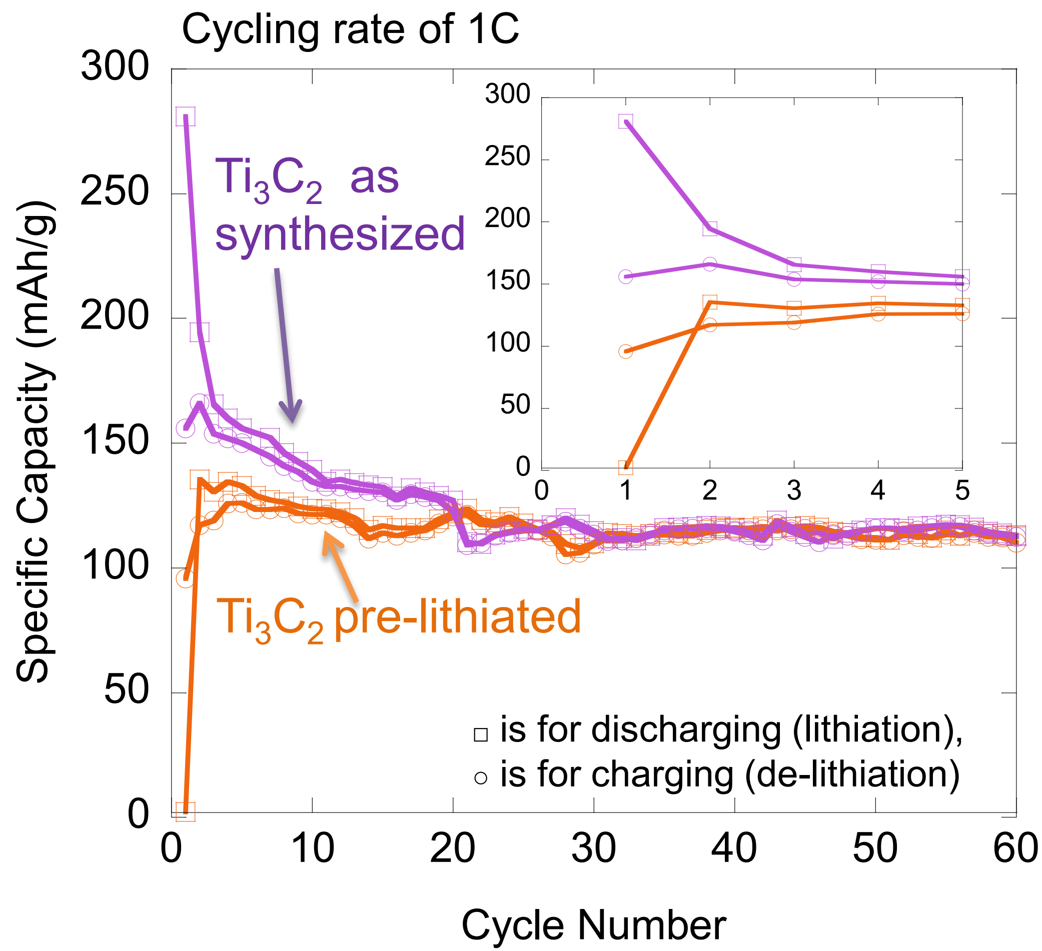
Pre-lithiation of Ti_3C_2 to minimize the 1st cycle irreversibility



Technical Accomplishments

Pre-lithiation of Ti_3C_2 to minimize the 1st cycle irreversibility

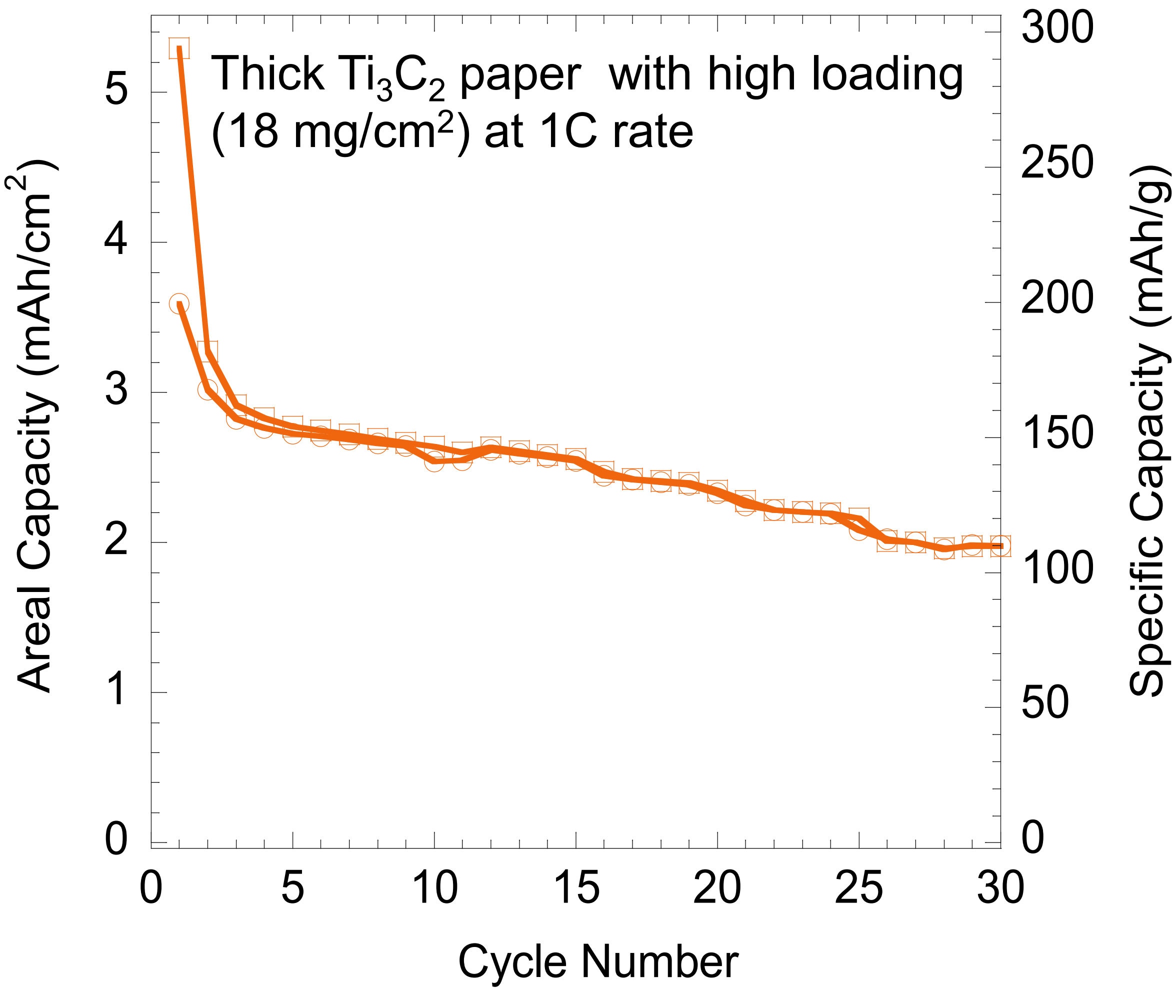
- Given that a large portion of the first cycle irreversibility is due to Li trapped between the layers, an attempt was made to pre-lithiate Ti_3C_2 using a simple and inexpensive proprietary process.
- The pre-lithiated Ti_3C_2 showed a low capacity for the first discharge cycle. However the reversible capacity after 30 cycles was identical to as-synthesized Ti_3C_2.
- This is an important result since it shows that the large 1st cycle irreversibility problem for the MXenes can be solved by a simple chemical pre-lithiation process.



Technical Accomplishments

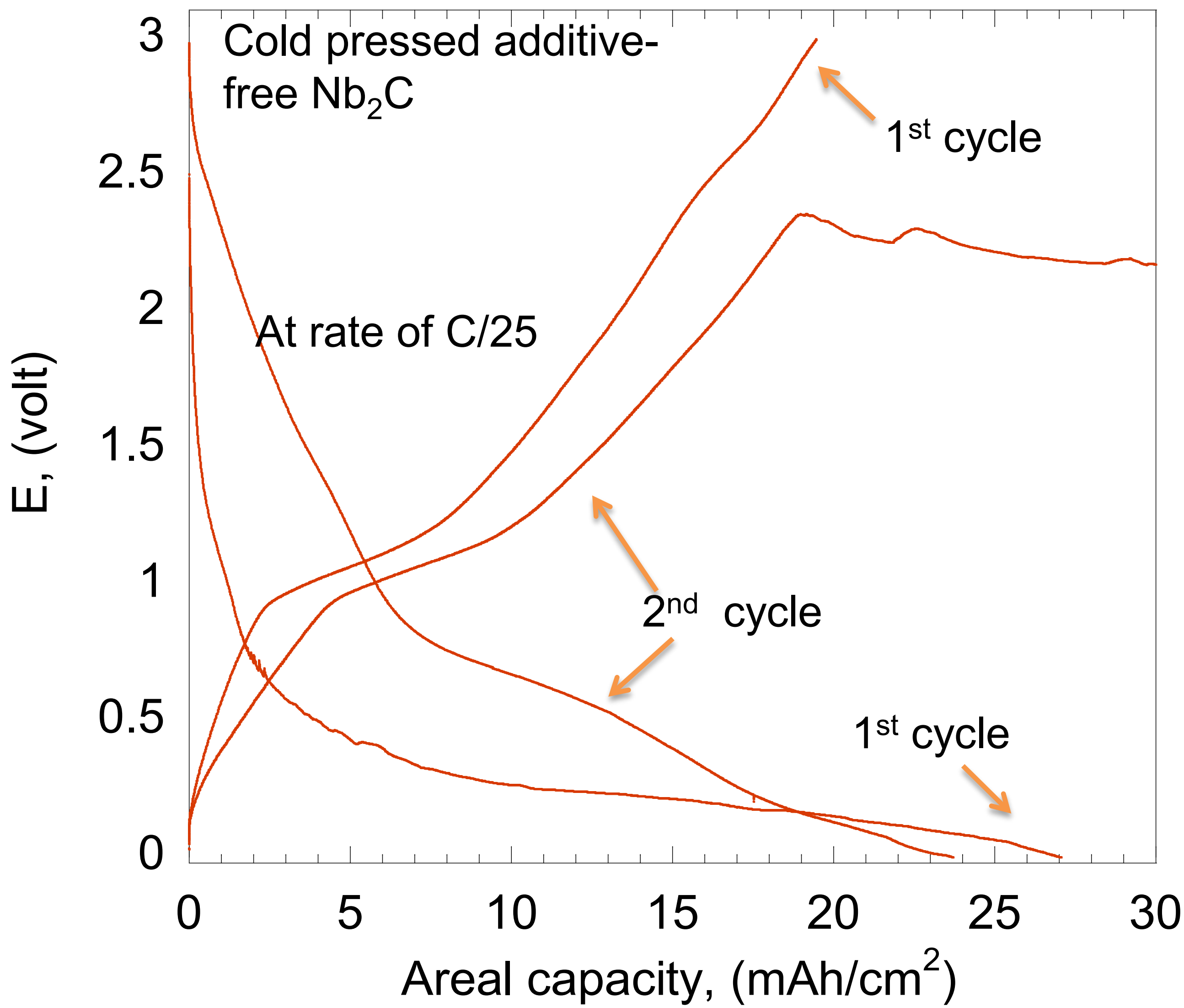
High loading of MXenes anodes

- Thick additive-free paper of delaminated Ti_3C_2 was tested as an anode in LIBs at a rate of 1C.
- Reversible areal capacity of ~2 mAh/cm^2 was obtained; this areal capacity is close to the areal capacity of graphite in commercial LIBs.



Technical Accomplishments

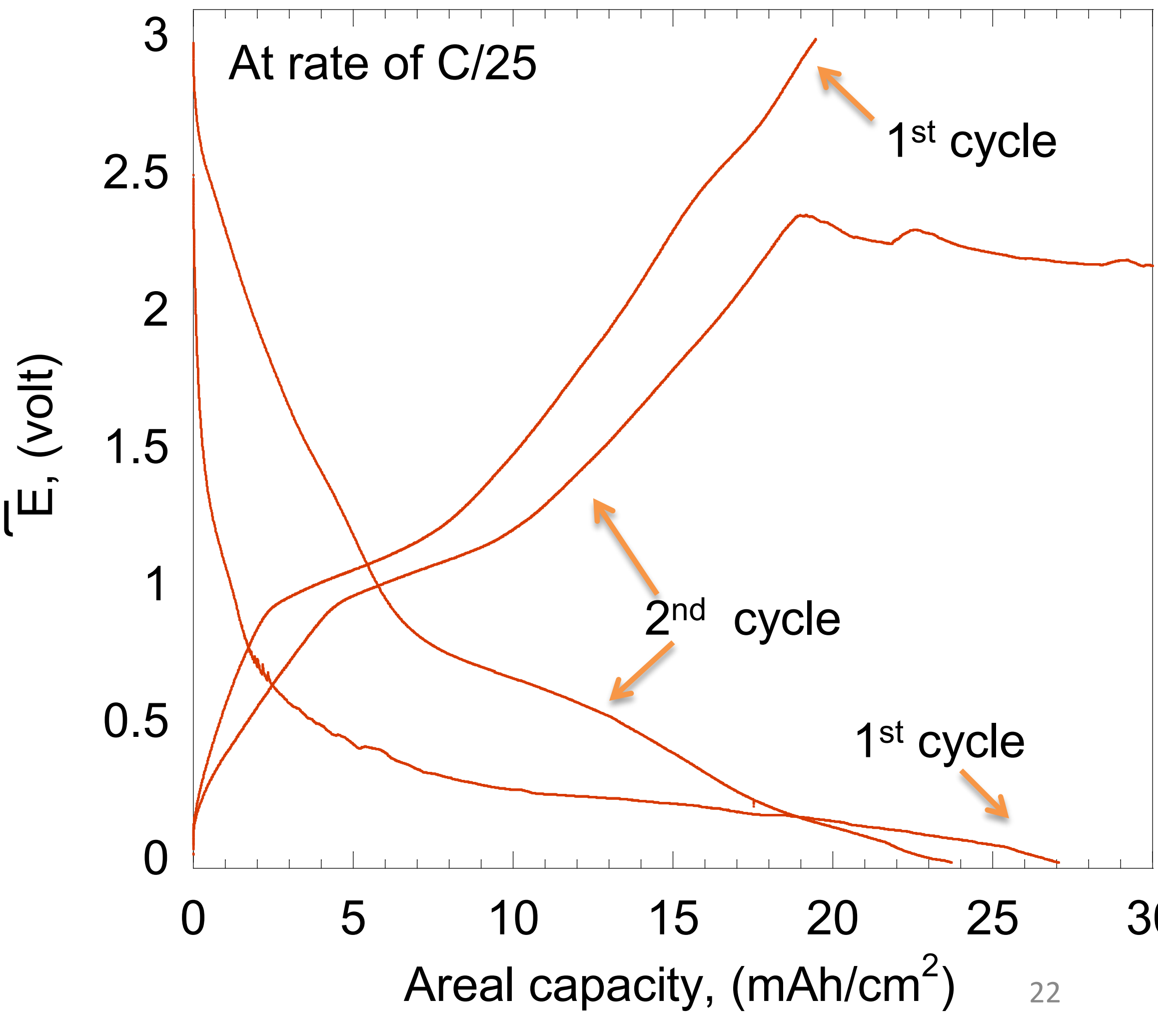
High loading of MXenes anodes



Technical Accomplishments

High loading of MXenes anodes

- Cold pressed additive-free Nb_2C MXene with loadings of more than 100 mg/cm^2 were fabricated.
- Coin cell failed during the 2nd charging cycle.
- The failure could be due to electrolyte depletion in the limited volume of the coin cell configuration.
- These results prove the concept that high loading can be achieved with MXenes.
- Further optimization is ongoing



Collaboration and Coordination

Externally supported collaborations

- Currently working with Prof. Vivek Shenoy (UPenn) on DFT simulation of lithiation and delithiation of different MXenes.
- Currently working with Dr. Ed Hagaman (ORNL) on NMR study of MXenes
- Collaborated with Dr. Sheng Dai (ORNL) on coating MXenes with carbon using CVD to minimize the energy loss in the first cycle due to SEI formation. No enhancement was observed. In-situ XRD showed that Li trapped between the layers is more problematic in case of MXene than SEI formation.
- Collaborated with Dr. Patrice Simon (Paul Sabatier University, Toulouse, France) on in-situ XRD studies.
- Collaborated with Dr. Lars Hultman (Linkoping University, Linkoping, Sweden) on HRTEM and EELS studies of MXenes.

Future Work

- Produce more M_2X MXenes, such as V_2C, because they have higher Li uptake than M_3X_2 or M_4X_3.
- Continue testing different MXenes in LIBs.
- Continue studying the lithiation and delithiation mechanisms in order to increase reversible capacity and minimize 1st cycle irreversibility.
- Combine different strategies to tackle the various challenges, such as combining pre-lithiation with fully delaminated MXene with or without C-onions.
- Develop techniques to produce cheap MXene phases

Summary

- Charge storage in MXenes is due to Li^+ intercalation between the MXene layers and not due to a conversion reaction.
- Different MXenes showed different Li uptakes and insertion potentials. Nb_2C showed a higher Li uptake than Ti_2C at a lower potential.
- Different C-additives and binders have been tested. The highest capacity obtained for a mixture of 80 wt.% Ti_3C_2, 10% PVDF & 10% carbon onions.
- Additive-free Ti_3C_2 anodes made by filtering a colloidal solution of delaminated flakes in water showed a capacity of 410 mAh/g at 1 C and 110 mAh/g, at 36 C for 200 cycles.
- Pre-lithiation of Ti_3C_2 solved the problem of 1st cycle irreversibility.
- MXenes anodes can be prepared with high loading (18 mg/cm^2) of Ti_3C_2 additive-free paper, producing 2 mAh/cm^2 capacity